INEEL

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INTEROFFICE MEMORANDUM

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Subject: APPROACH TO SIMULATION OF ACTINIDES FOR THE OU 7-13/14
                BASELINE RISK ASSESSMENT - LCH-04-01

For the OU 7-13/14 remedial action investigation, a baseline risk assessment must be conducted to evaluate the risk posed by waste buried in the Subsurface Disposal Area. For the groundwater pathway, there is currently no risk posed by actinide radionuclides (U, Np, Pu, and Am) in the Snake River Plain Aquifer. However, future risk must be predicted to assist in reaching a remedial action decision that is protective of human health and the environment. A computer simulation is the planned approach to be used to calculate future risk by the groundwater pathway. Numerous parameters describing many processes are needed as input for the computer simulation model. This memo discusses geochemical parameters that affect contaminant fate and transport for the predictive computer simulation.

Schedule is acknowledged to be a significant factor that must be considered in evaluating what can be done in support of the risk assessment computer simulation. The baseline risk assessment must be completed by the end of the fiscal year (September 2001) and work on the computer simulation has already started. Therefore, no significant changes in approach can be accommodated in the computer simulation at this time without threatening regulatory schedules.

In this memo, I will make some recommendations about how the geochemical factors affecting transport could be handled for the baseline risk assessment, and beyond. First, I will describe the important geochemical factors that affect contaminant fate and transport. These geochemical factors can be divided into environmental geochemical factors and contaminant specific geochemical properties. A brief summary is then provided on the anticipated geochemical conditions at the SDA. Some of this is based on site-specific information, but much is based on scientific conjecture. Two levels of approach to geochemical treatment of contaminant transport are presented. The simplest method is to use adsorption isotherms (linear, Freundlich, Langmuir), the more complex method is to use reactive transport modeling. Finally, a matrix is presented summarizing the various geochemical factors and a strategy to address these factors immediately, and over the next few years.

The groundwater exposure pathway can be divided into three sections – the source term (buried waste), the vadose zone, and the Snake River Plain Aquifer. This memo will address only transport in the vadose zone under the SDA. The source-term model has to address all of the same geochemical factors discussed here for the vadose zone, as well as other information. The source term deserves a separate evaluation. Once a contaminant reaches the Snake River Plain Aquifer, transport will be primarily through interflow zones and fractures in the basalt. A receptor can be exposed to the radionuclide by ingestion of groundwater at any location, including very close to the SDA. Because of this, retardation during transport in the aquifer is of much less concern than retardation during transport through the vadose zone.

Summary of Geochemical Factors in the Subsurface Environment

Geochemical processes in the subsurface were lumped into a single parameter for the interim OU 7-13/14 risk assessment. This single parameter was an equilibrium, reversible distribution coefficient, referred to as a Kd. Surface adsorption reactions play an important role in the fate and transport of contaminants, and if the Kd value is determined under conditions representative of the site (representative in terms of site-specific geochemical factors), then the partition coefficient can be a simple approach to incorporate geochemical reactions into a risk assessment computer simulation. However, if conditions at the site are changing, or if there are significant geochemical gradients, then the problem becomes much more complicated. A single partition coefficient assumes that geochemical conditions at the site remain static. When leachate migrates downward from the bottom of the pit into underlying sediment and basalt, there is likely to be an appreciable change in geochemical environment. Reducing conditions in the pit are replaced by oxidizing conditions in the vadose zone, for example. Under such strong geochemical gradients, many complex geochemical reactions take place that cannot be accommodated by a single partition coefficient.

There are many other uncertainties in the risk assessment model. It has been stated that because of the uncertainty in the flow model, a low Kd value is justified. A geochemical parameter cannot be used to address uncertainties in other portions of the flow model.

The fate and transport of contaminants are affected by a number of factors that comprise the subsurface geochemical environment. This section summarizes the geochemical factors in the subsurface environment. The factors to be discussed are: redox state; water chemistry; organic complexing; facilitated transport; and subsurface heterogeneity.

Redox State. The first geochemical environmental factor is the redox state. Redox refers to the reduction / oxidation state of the environment. The redox condition is important for actinides because most of the actinides can change valence state depending on the redox state of the environment. This then affects the solubility and mobility of the actinide. Knowledge of the redox state defines the expected valence state of the actinides.

Solution Chemistry. The chemistry of the water in the soil pores can affect the mobility of contaminants. Cations in solution can compete for adsorption sites on the soil; anions can form aqueous complexes with the actinides, which keeps the actinide in solution and inhibits adsorption to solids; the pH of the solution affects anion complexing and controls the electrical charge on the surfaces of soil minerals. At low pH, the surfaces of minerals become positively charged, which repels the positively charged actinide cations in solution.

Organic Complexes. Actinide elements can form aqueous complexes with organic molecules in solution. The actinide-organic complex keeps the actinide in solution and inhibits partitioning to solid phases. Solutions emerging from pits and trenches are likely to contain a large number of organic molecules, some of which have the potential to complex actinides (Cleveland and Mullin 1993). Of particular concern are chelating agents, such as ethyldiaminetetraacetic acid (EDTA), which were used in decontamination solutions at Rocky Flats (INEEL 1998). Column studies conducted at Clemson University (Fjeld, Coates, and Elzerman 2000) showed that EDTA mobilized significant fractions of actinide elements that were immobile when EDTA was not present. Volatile chlorinated solvents, such as carbon tetrachloride, are not good complexing agents, and so the volatile organic compounds are not a concern in this respect.

Facilitated Transport. At a number of locations, contaminants have been found to move more rapidly than expected. This phenomenon occurs in a number of different disciplines including the transport of pesticides through agricultural soils and the transport of radionuclides from nuclear testing at the Nevada Test Site. Contaminants can form colloidal particles or be adsorbed onto colloidal particles. Actinides such as plutonium and americium are particularly susceptible to this because of their low solubility.

Colloids are themselves, susceptible to retardation by mechanisms such as adsorption and straining (McDowell-Boyer, Hunt, and Sitar 1986). Some colloidal particles, however, may be very mobile because of surface charge characteristics and size (Sun et al. 2001). In column experiments conducted at Clemson University using INEEL sediment (Fjeld, Coates, and Elzerman 2000), a very small percent of quatravalent actinides traveled through columns with little or no retardation. Facilitated transport on colloids was identified as a possible mechanism.

Heterogeneity. The subsurface at the SDA consists of a sequence of layers of sediment and basalt. There are appreciable variations in material properties vertically and horizontally. Geochemical reactions are strongly dependent on the surface area and mineralogy of the geologic materials. Lateral and vertical variations in mineralogy and surface area result in a very non-homogeneous distribution of retardation capacity in the subsurface. Adsorption of a contaminant from solution is dependent on the chemical properties of the contaminant, and the number and type of adsorption sites in the sediment. The traditional approach of measuring an empirical Kd has lumped both chemical and material properties into a single parameter. Acknowledgement of spatial variation implies a separation of chemical properties of the actinide and adsorption properties of the geomedia.

In addition to the heterogeneity in the geologic media, there are heterogeneities in the other components of the geochemical environment. Water chemistry is not constant, for example, under all parts of the SDA. Therefore, geochemical approaches that either ignore, or empirically treat, these sources of variation carry inherent short comings for developing a defensible risk assessment model.

Summary of Actinide Geochemical Properties

The four actinides of interest are uranium (U), neptunium (Np), plutonium (Pu) and americium (Am). Geochemical properties of interest are the stability of valence states, the solubility of the actinide, and the strength of partitioning between aqueous solutions and minerals.

Uranium. Uranium occurs in two valence states in nature, U(IV) and U(VI). Uranium (IV) occurs under reduced conditions and uranium (VI) occurs in oxidized conditions (Figure 1). Uranium (IV) is very insoluble forming uraninite (UO_2) or a mixed valence oxide phase like $UO_{2.25}$ or $UO_{2.33}$. Uranium (VI) is much more soluble and mobile. Uranium (VI) also forms soluble complexes with carbonate anions in natural waters. Figure 1 shows that the aqueous complex $UO_2(CO_3)_2^{-2}$ is the predominant form of uranium between pH 7 and 8 in an oxidized environment. Numerous investigations of the adsorption of uranium on soils and minerals have shown that carbonate complexing appreciably reduces adsorption of uranium (Waite et al 1994; Pabalan and Turner 1997; Pabalan et al 1998; Fjeld, Coates, and Elzerman 2000).

Adsorption studies conducted with uranium batch tests and columns (Newman et al. 1995; Fjeld, Coates, and Elzerman 2000) show that uranium is mobile in oxidized conditions and water high in carbonate. Measured Kd values range from 3 to 10 ml/g for U(VI). These studies were all conducted on a composite interbed material. Kd values measured on a range of 14 interbed samples from the vicinity of the SDA (Fjeld, Coates, and Elzerman unpublished data) range from 5.9 to 36.9 ml/g (Table 1). More details on these tests are provided in the Appendix to this memo. Uranium mobility is dependent on redox state with uranium being much more mobile in an oxidized environment than in a reduced environment. The mobility of uranium is enhanced by the presence of carbonate in solution. Uranium carbonate complexes in solution can effectively compete for uranium (VI) with surface adsorption sites. Uranium is least mobile in a reduced environment and most mobile in an oxidized environment high in carbonate.
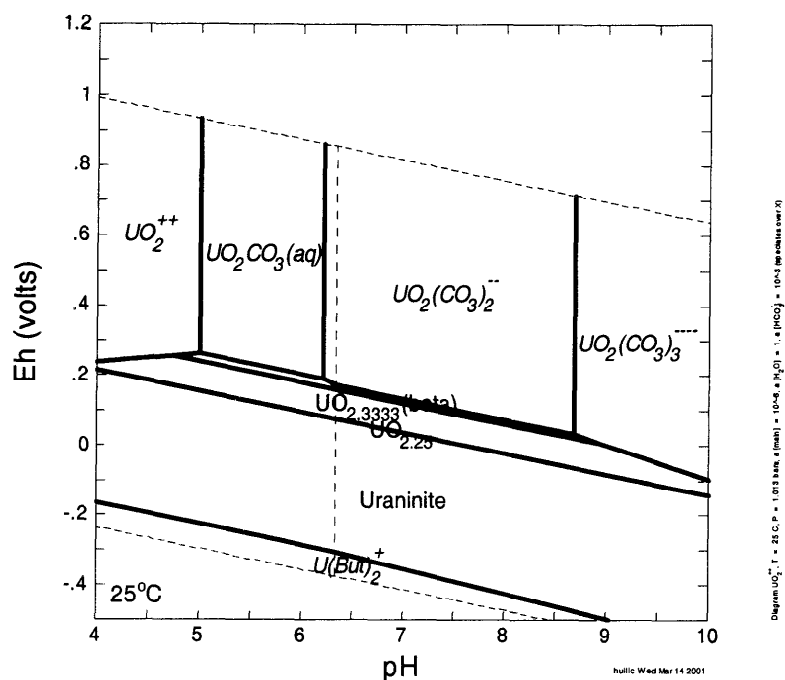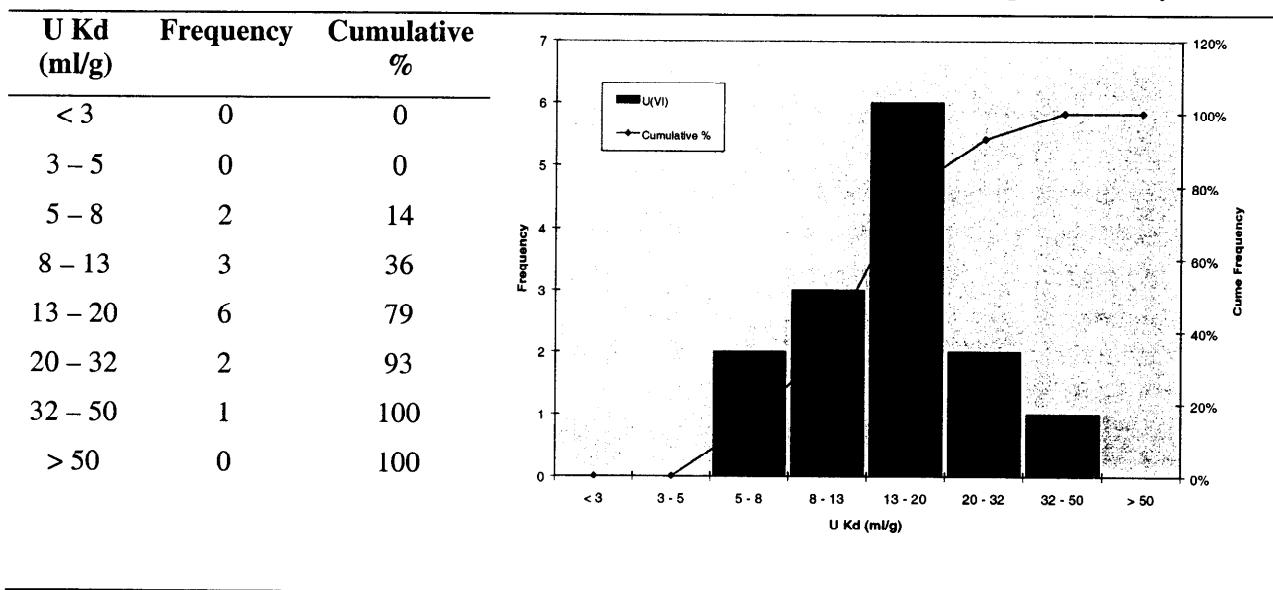
Figure 1 Eh-pH diagram for uranium showing presence of solid phase fields at low Eh values and predominance of dissolved uranium carbonate complexes at high Eh. Fields labeled with italicized text indicate soluble species dissolved in water. Fields labeled with upright text indicate solid mineral phases. The upper most diagonal dashed line is the upper stability limit of water and represents oxidized conditions. The lower most diagonal dashed line represents the lower limit of water stability under reduced conditions. When Eh values are above 0.2 V between pH 7 and 8, uranium will be in the oxidized valence state (VI).

Neptunium. Neptunium can be present in the Np(IV) and Np(V) valence states in the environment (Figure 2). Np(V) is the predominant aqueous species except at very low redox potential. Neptunium carbonate complexing is relatively unimportant except at very high pH values (pH > 8.5).

Neptunium Kd values have been measured by Fjeld, Coates and Elzerman (2000, and unpublished data) for composite INEEL sedimentary interbed material, and on 14 samples of interbed material. The column Kd values for the composite sediment ranged from 24 to 39 ml/g. For the 14 interbed samples, Kd values ranged from 5.9 to 100 ml/g (Table 2). Additional data from the batch partition coefficient experiments is included in the appendix.

Table 1. Cumulative frequency distribution of uranium Kd values measured on SDA sedimentary interbed samples (Fjeld, Coates, and Elzerman unpublished data). The size of the bins used in the frequency distribution of this and the other tables presented, increase in size logarithmically.

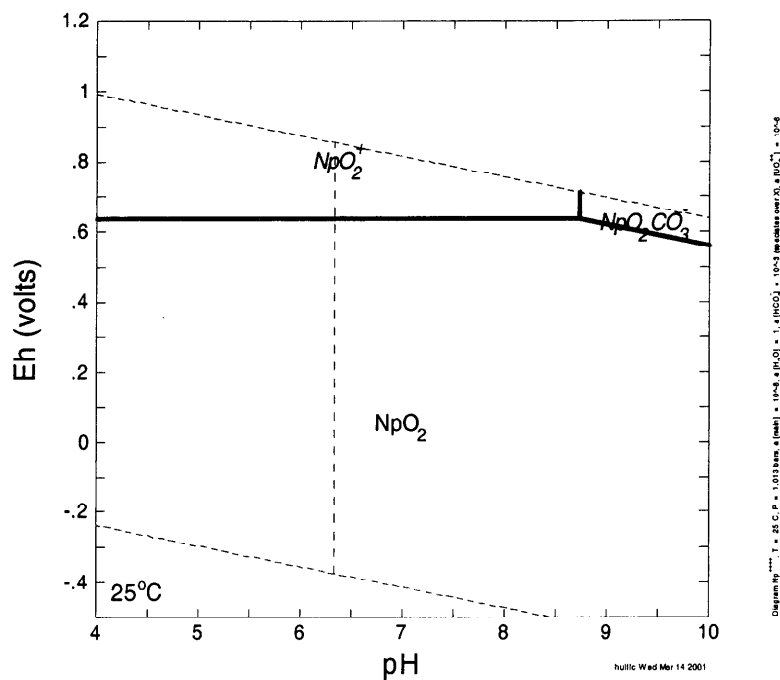| U Kd (ml/g)	Frequency	Cumulative %
< 3	0	0
3 – 5	0	0
5 – 8	2	14
8 – 13	3	36
13 – 20	6	79
20 – 32	2	93
32 – 50	1	100
> 50	0	100

Figure 2 Eh-pH diagram for neptunium showing that neptunium (V) is the stable form of neptunium in oxidized conditions, but that reduction to a fairly insoluble neptunium (IV) solid phase occurs under mildly reduced conditions.

Table 2. Cumulative frequency distribution of neptunium Kd values measured on SDA sedimentary interbed samples (Fjeld, Coates, and Elzerman unpublished data).

Np Kd (ml/g)	Frequency	Cumulative %
< 5	0	0
5 – 10	1	7
10 – 20	2	21
20 – 40	7	71
40 – 80	1	79
80 – 160	3	100
> 160	0	100
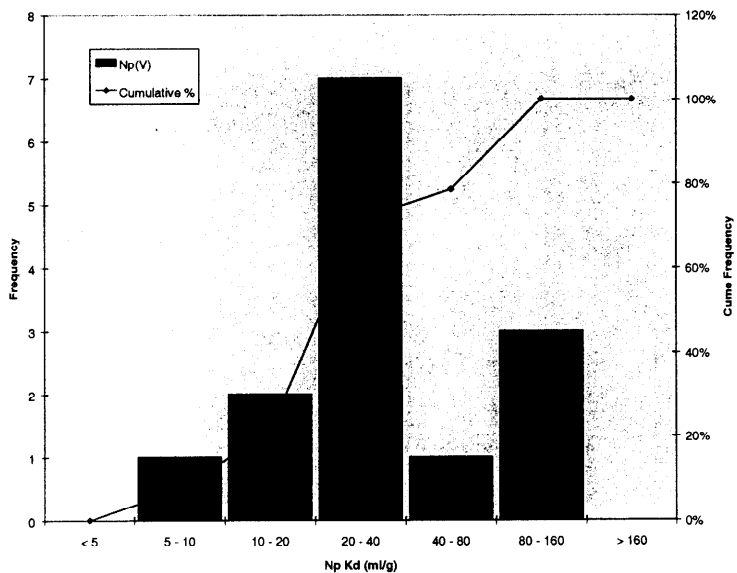
Neptunium will be more mobile in an oxidized environment than in a reduced environment. In even mildly reducing environments, neptunium can be reduced from the pentavalent form to the tetravalent form with subsequent precipitation of oxide or hydroxide. Aqueous complexes with anions play a secondary role in the mobility of neptunium.

Plutonium. Plutonium has a very complicated redox chemistry. While thermodynamic calculations predict stability fields for the different oxidation states of plutonium, laboratory experiments indicate that multiple oxidation states of plutonium frequently coexist in solution. In oxidized aqueous solutions, plutonium (V) (PuO_2^+) is calculated to be the stable valence of plutonium except under very acidic conditions (Figure 3). Carbonate complexing can stabilize plutonium (VI) in very oxidized environments at pH values greater than about 7.5. Under even mildly reduced conditions however, plutonium (IV) in the form of $Pu(OH)_4(aq)$ becomes the predominant form of plutonium in solution. When solid phases are considered, the extremely low solubility of PuO_2 dominates the distribution of plutonium (Figure 4). Reduction of Pu(VI) and Pu(V) to Pu(IV) and precipitation of PuO_2 can occur under any redox condition at neutral pH.
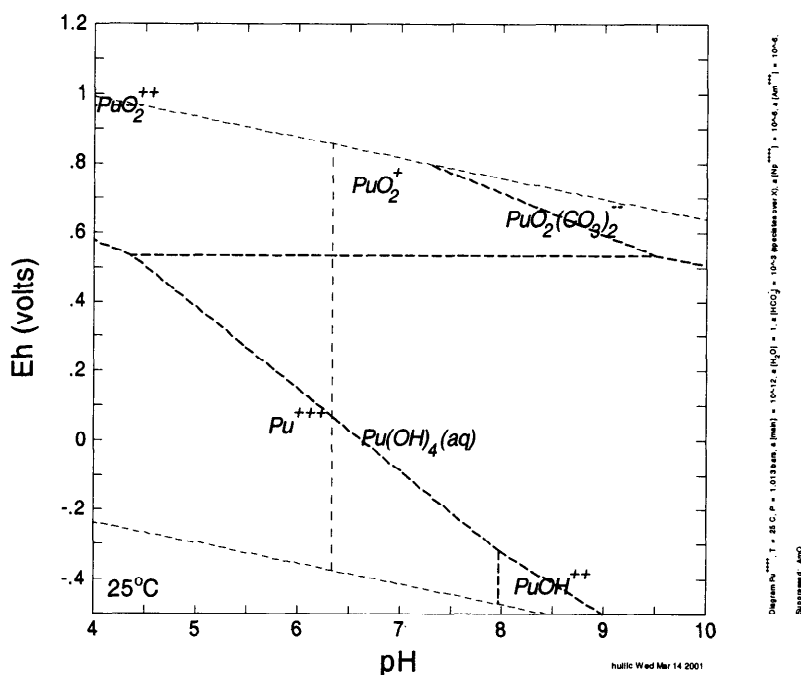

Figure 3 Eh-pH diagram for aqueous plutonium species showing that plutonium (V) is the prevalent oxidation state of plutonium in oxidized conditions and that plutonium (IV) is stable in reduced conditions a neutral and alkaline pH values.
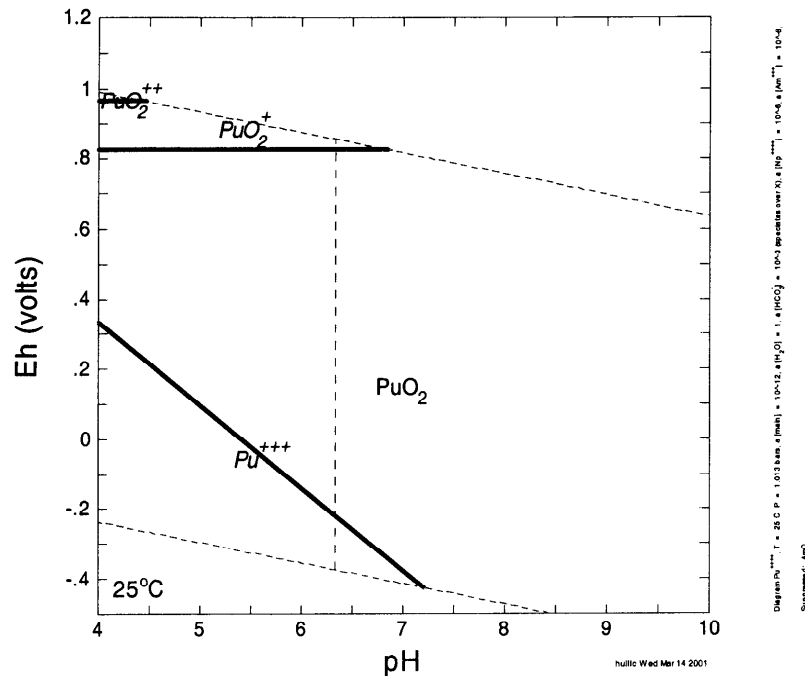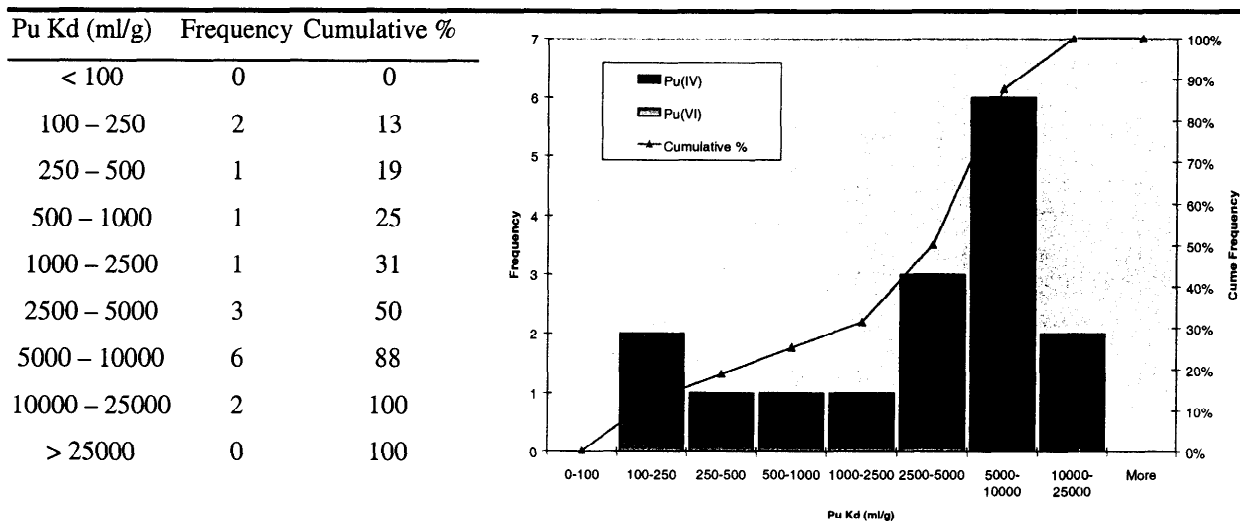
Figure 4 Eh-pH diagram of plutonium with solid phases showing that PuO2 is so insoluble that the Pu(IV) compound dominates the solubility of plutonium under all redox conditions at neutral and alkaline pH.

Studies of plutonium oxidation state distribution in water show that plutonium (VI) will remain stable in water typical of INEEL groundwater in the absence of solids or at low suspended solids concentrations (Cleveland and Mullin 1993; Newman et al 1995). In the presence of high suspended solids or in column studies, however, plutonium is reduced from Pu(VI) or Pu(V) to Pu(IV) (Newman et al 1995; Fjeld, Coates, and Elzerman 2000). In a column experiments, investigators at Clemson University ran hydrogen peroxide through the column before adding plutonium to the column. Even when the column was preoxidized, the INEEL sedimentary material reduced the plutonium to Pu(IV).

The frequency distribution of measured Kd values for plutonium by Newman et al (1995) is shown in Table 3. The data from Newman et al are used in this figure because the starting valence state of (VI) or (V) was determined. There is a very broad range of partition coefficients measured ranging from 110 ml/g to a maximum measured plutonium partition coefficient of 22,000 ml/g. None of the results from column experiments are included in Table 3 because breakthrough did not occur in any of the column experiments. Therefore, Kd values could not be determined from the column results. Partition coefficients for sedimentary interbed material are lower than for surficial sediments. Partition coefficients for Pu(VI) starting solutions are lower than for Pu(V) starting solutions.

The hypothesis derived from these results is that plutonium (V) is more readily reduced to plutonium (IV) than is plutonium (VI). Surface soils containing more plant detritus and an active microbial community are better at reducing plutonium (V) or (VI) to plutonium (IV). In sedimentary interbed material, at low suspended solids concentrations, with low organic matter content, plutonium (VI) remains stable in solution, and is sparingly adsorbed to the solids. The great amount of variation in measured Kd values for plutonium can be attributed to the variation in the reduction of the initial plutonium in solution to plutonium (IV). If the plutonium stays in the hexavalent oxidation state, the Kd value will be low (100 to 700 ml/g). If plutonium is reduced to the quatravalent oxidation state, then the Kd value will be greater than 5100 ml/g. Values in between may indicate partial reduction of the plutonium.

Table 3. Cumulative frequency distribution of plutonium Kd values measured on INEEL soils and sedimentary interbed materials by Newman et al (1995)

Pu Kd (ml/g)	Frequency	Cumulative %
< 100	0	0
100 – 250	2	13
250 – 500	1	19
500 – 1000	1	25
1000 – 2500	1	31
2500 – 5000	3	50
5000 – 10000	6	88
10000 – 25000	2	100
> 25000	0	100

The best Kd value to select for plutonium depends strongly on the anticipated valence state of plutonium. Studies by Newman et al (1996) and Fjeld, Coates, and Elzerman (2000) on INEEL materials indicate that plutonium (V) and (VI) are not stable in contact with INEEL sediment or soil materials when there is a high solids to solution ratio. In some batch experiments, in the presence of organic matter in the sample, in column studies, plutonium is reduced during the experiment. Based on these experimental results, it is reasonable to assume that plutonium will be present in the quatravalent state in the subsurface at the SDA. Under these conditions, where the valence state was reported, partition coefficients are above 5,100 ml/g. These findings represent a case for the use of a Kd value of 5,100 ml/g for plutonium at the SDA as a number that can be shown to be conservative (near the bottom of the range of reduced plutonium adsorption coefficients) yet representative of conditions at the site (within the range of measured values).
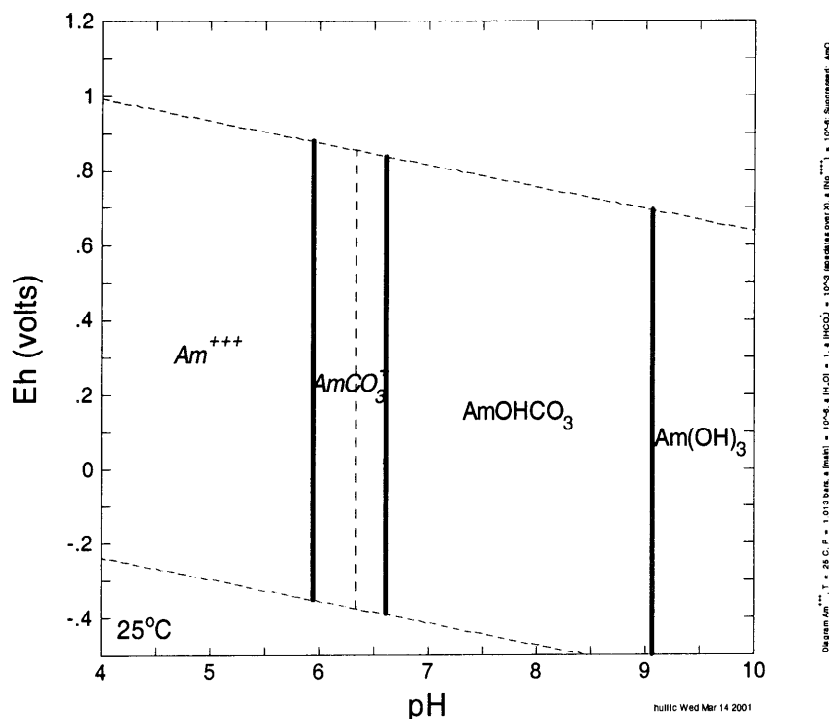
Figure 5 **Eh-pH diagram for americium showing that americium is present in the trivalent oxidation state under all redox conditions. Insoluble hydroxides and hydroxycarbonates control the solubility of americium at neutral and alkaline pH.**

Americium. Americium is found only in the trivalent oxidation state in the environment. There is an insoluble americium hydroxy-carbonate solid that forms under neutral pH conditions (Figure 5). Americium partition coefficients measured on a composite SDA sedimentary interbed material ranged from 450 to 1100 ml/g. In column experiments (Fjeld, Coates, and Elzerman 2000), Am does not breakthrough at the end of the column during the duration of the experiment, and so the column experiments only indicate the Kd for Am is greater than 250 ml/g.

Discussion. The analysis of the geochemical properties of the actinides indicate that the four actinides do not have the same geochemical characteristics. Americium and plutonium form very insoluble mineral phases at neutral pH in oxidized aqueous solutions. Investigators at Clemson found that test solutions made in the laboratory for plutonium and americium resulted in precipitation of solids that could be filtered from solution (Fjeld, Coates, and Elzerman 2000). Therefore, the actinides can be divided into two groups – uranium and neptunium; which will be soluble in oxidized conditions; and plutonium and americium, which will have low solubility and could be more susceptible to transport in particulate form. Uranium and neptunium are transported through columns during laboratory experiments, and show breakthrough curves that can be described using an adsorption model. Americium and plutonium do not breakthrough during column experiments and are significantly retarded relative to the movement of water. Americium and plutonium, however, show small fractions of material that are continually released from columns. A transport mechanism such as facilitated transport on colloids would seem to be a better model to describe the migration of plutonium and americium.

Brief Description of the Subsurface Environment at the SDA

This section discusses what is known about the subsurface environment at the SDA with regard to fate and transport processes. This discussion is extremely brief, and does not include the full documentation and backup information that would be needed in a baseline risk assessment. The organization follows the organization used in the general discussion of the geochemical factors that affect transport: redox state; water chemistry; organic complexing; facilitated transport; and subsurface heterogeneity.

Redox State. In terms of redox potential, there are very sparse data on the presence of oxygen in the vadose zone. The following table (Table 4) shows the available field measurements. Samples were collected with as minimal disturbance as possible, and a micro-winkler dissolved oxygen titration performed immediately following sample collection in the field. The concentrations are appreciable, and not (in my experience) consistent with air contamination during sampling. Note that lysimeter DL03 is at a depth of 227 ft, providing a definite rationale for assuming oxidizing conditions under the SDA at the 240-ft interbed. I believe that these measurements are representative of conditions in-situ. This is the natural environment (or was the natural environment 10 years ago, as far as I know there are no recent data on dissolved oxygen).

Other chemical parameters are consistent with oxidizing conditions. Iron and manganese concentrations are consistently very low, natural uranium is present in measurable quantities, sulfate is ubiquitous in samples, and nitrate is present at many monitoring locations. Basalt contains no organic matter and the detrital sediments deposited in a desert environment are also very low in organic matter (0.05 to 0.17% organic carbon). There is appreciable air permeability in the basalts permitting diffusion of oxygen through the system. The Snake River Plain Aquifer contains dissolved oxygen (see for example Table 4-2 in the USGS Review of the OU 7-13/15 Interim Risk Assessment [USGS 2000]).

Table 4 Dissolved oxygen measurements from suction lysimters at the SDA.

Well	Lysimeter	Depth (ft)	Date	DO (mg/L)
C01	L19	17.67	8/29/89	8.3
TW1	DL03	226.92	6/16/88	7.8
W02	L01	14.00	6/17/88	4.8
W03	L02	10.50	10/5/89	4.2
W04	L03	24.50	6/11/86	6.5
W04	L04	15.42	8/31/89	6.2
W05	L24	15.92	9/3/87	7.5
W08	L12	22.08	7/27/89	4.9
W09	L23	14.83	7/24/89	7.0
W13	L29	14.00	9/30/88	4.3

Solution Chemistry. The chemistry of water in the vadose zone at the SDA has mainly been measured by the use of suction lysimeters. Limited sampling of perched zone monitoring wells has also been conducted. During the mid-to-late 1980s, a network of suction lysimeters was installed in surficial sediment and sedimentary interbeds to monitor soil water chemistry (Laney and Minkin 1988). Water samples collected from these lysimeters can be used to define the expected soil water chemistry for pore water in the SDA. Similar analyses have been conducted before by Dicke (1997) and Hull and Pace (2000), but for different objectives. The sampling results provide data that show the chemistry of water under the SDA is very heterogeneous.

Data in the first part of Table 5 are for lysimeters installed in interbeds and for perched water monitoring wells. These data represent the water in the vadose zone under waste that would affect the migration of contaminants. The first eleven lines in the table show water with very high total dissolved solids with thousands of mg/L of sodium and chloride. The next six lines show a water much lower in dissolved

solids. The next two lines of the table show the composition of water used in laboratory experiments conducted by Newman et al. (1995) and Fjeld, Coates, and Elzerman (2000).

Water on the west end of the SDA (at Well USGS-92 and Lysimeter DL06) and in deeper interbeds at the east end of the SDA (at Well DL03) are low in dissolved solids. A tracer test conducted by the USGS in 1999 showed that tracer added to the spreading areas west of the RWMC migrated laterally to well USGS-92. Therefore, the low dissolved solids water probably reflects a significant component of recharge from the spreading areas.

Water on the east and north of the SDA is much higher in salt content than water at the west end of the SDA (Table 5). This higher salt content is the result of a brine solution applied to roadways in the SDA to suppress dust. The link to the brine as the source is identified by the bromide to chloride ratio. Waste disposal operations at the SDA generated large quantities of airborne dust from heavy equipment moving along dirt roads. Magnesium chloride brine was applied to selected RWMC roadways in 1984, 1985, 1992, and 1993 to control airborne dust. The brine migrated very rapidly in the soil water and was detected in some of the suction lysimeters by 1988. Ten years later in September 1998, samples collected from Lysimeters DL01, DL02, and DL04 showed that levels of sodium and chloride remained very high in these lysimeters, even though brine has not been applied at the SDA since 1993.

From this available data, it appears that there are at least two very different water types under the SDA. A comment from the USGS (USGS 2000) in their review of the Interim Risk Assessment (Becker et al. 1998) stated that use of the adsorption isotherm approach will require demonstration that the geochemical conditions in the vadose zone were reasonably stable. The large difference in water chemistry measured in the deep lysimeters indicates that geochemical conditions are far from stable in the vadose zone under the SDA. Because there are (at least) two different geochemical regimes in the vadose zone under the SDA, a single, representative water sample cannot be identified.

There is a very large difference in cation concentrations between the two water types, indicating that the high TDS water could inhibit retardation by competing for adsorption sites. The carbonate concentrations in the two waters are similar. There is a big difference in pH. However, a pH value of 7.1 is not low enough to inhibit adsorption of most metals. What may be more significant is that the high pH of the low TDS water could contribute to more carbonate complexing of actinides in the low TDS water. Water chemistry is highly variable under the SDA.

The chemistry of synthetic water used in laboratory batch adsorption experiments and column studies by Newman et al. (1995) and Fjeld, Coates, and Elzerman (2000) differ appreciably from either of the observed water chemistries. In particular, the Newman et al water underestimates the carbonate concentration, and Fjeld, Coates, and Elzerman water overestimates the carbonate concentration. Because carbonate complexing is an important consideration for adsorption, these differences may appreciably affect adsorption.

Table 5. Chemical composition of water in the vadose zone at the SDA as measured in suction lysimeters and perched water monitoring wells.

Well	Lysimeter	Depth (ft)	Date	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	HCO3 (mg/L)	Cl (mg/L)	F (mg/L)	SO4 (mg/L)	Br (mg/L)	NO3 (mg/L)	Field pH	Temp (°C)
D06	DL01	88.0	9/9/98	691	426	1020	43.5	264	3420		1860	8.40	110.00	7.31	20.3
D06	DL02	44.0	6/17/88	707	678	2675	55.9	177	5270	0.39	2370	11.50		7.12	18.4
D06	DL02	44.0	8/2/88	708	688	2757	57.0	183	5420	<0.05	2390	11.40		7.78	14.8
D06	DL02	44.0	9/29/88	680	679	2774	60.0	193	5567	0.41	2375	7.30		7.15	12.4
D06	DL02	44.0	7/27/89	724	735	2937	61.5	229	5730	0.40	2612	10.50		7.27	20.3
D06	DL02	44.0	8/31/89	755	757	3035	62.1	221	5860	0.38	2575	11.30		7.12	14.0
D06	DL02	44.0	9/9/98	752	822	3180	86.5	449	7140		4380	12.80	94.00	7.55	18.5
TW1	DL04	101.7	6/16/88	804	417	595	29.7	182	2700	0.53				6.98	18.2
TW1	DL04	101.7	8/2/88	911	494	682	32.0	180	2990	<0.05	1090	33.00			
TW1	DL04	101.7	9/9/98					200	3280		489	6.10	61.00	6.98	15.8
	High TDS		Median	724	679	2757	57	197	5345	0.4	2375	11.3	94	7.15	18
TW1	DL03	226.9	6/16/88	33	8	222	3.1								
D15	DL06	97.9	6/16/88	53	18	254	3.8	284	135	0.90	314	3.60		8.10	19.8
D15	DL06	97.9	8/2/88	38	7	258	4.6	275	89	0.95	287	2.50			
D15	DL06	97.9	9/27/88	35	6	256	4.1	278	152	0.90	233				
	USGS 092	213.0	10/29/76	29	17	120	12.0	290	81	0.4	64	0.3		8.39	13.5
	Low TDS		Median	35	8	254	4	281	112	0.9	260	2.5		8.25	17
	Newman et al. (1995)			11.5	8.3	19.7	9.8	96.6	18.9	.5	23.4	-	-	8.0	
	Fjeld et al. (2000)			10.5	17.5	566	10	747	220	20	350	-	-	8.2	

Organic Complexes. Laboratory tests at Clemson University using EDTA, an organic complexing agent (Fjeld, Coates, and Elzerman 2000), showed that EDTA could greatly enhance the mobility of actinides. An inventory of complexing agents, such as EDTA, used at the Rocky Flats Plant (INEEL 1998) indicates that organic complexing agents are likely to be present in the waste. No sampling or analysis has been done to test for the presence of complexing agents in the subsurface. In the absence of information, the possibility of transport as organic complexes cannot be fully evaluated.

Facilitated Transport. There are no data on colloid formation or facilitated transport at the SDA. The only information available comes from column studies. In column studies of plutonium transport by Miner, Evans, and Polzer (1982), by Newman et al (1995), and by Fjeld, Coates, and Elzerman (2000), plutonium was mainly bound strongly to the sediment in the column. However, there was a small fraction (generally much less than 1%) of the plutonium that was transported through the column fairly rapidly. This fraction seems to be the result of a continuous release of a small fraction of plutonium rather than a highly mobile portion of plutonium that was present initially.

For americium and plutonium, transport in the dissolved phase may not be an important mechanism. The best conceptual model for americium and plutonium seems to be the formation of an insoluble solid phase which is mostly filtered out of solution. This gives the appearance of a large Kd value in either column experiments or batch experiments. There is a small, but continuous release of the solid in colloidal form that migrates with the water. Column experiments conducted by Evans, Miner, and Polzer (1982) and at Clemson University (Newman et al 1996; Fjeld, Coates, and Elzerman 2000) reproduce this slow release of a small fraction of the actinide over time. Because of this, a tiny fraction of the actinide could be moving with little retardation through the vadose zone. Where retardation could be quantified for the mobile fraction, the calculated Kd value is generally on the order of 0.5 to 1 ml/g. The bulk of the actinide is very immobile. Additional development on computer models, processes, and monitoring will be needed to have a defensible prediction of americium and plutonium migration.

Heterogeneity. There undoubtedly exists appreciable spatial variation in material properties in the subsurface. To date, there has been no attempt to systematically characterize material properties and to develop spatially distributed parameters for computer simulation models. Past models (most recently Magnuson and Sondrup 1998) used average properties for all subsurface materials. To adequately address the issue of preferred flow paths, spatially distributed material properties are needed. It is not possible with the current level of information to adequately characterize the spatial distribution of material properties for geochemistry.

If spatial variation is to be addressed, the amount of data collection needed increases appreciably over an average property approach. Both horizontal and vertical changes in material characteristics must be measured. An approach to estimating spatial data would have to be selected. The most defensible method commonly used is kriging. For kriging to be used, the spatial correlation distance of material properties must be defined. This requires sampling at very close intervals.

Approaches to Incorporating Geochemistry into the Transport Model

The transport and fate of contaminants in geologic material are dependent on chemical and physical processes that govern the distribution of contaminants between the solid and aqueous phase. Adsorption of dissolved species onto solid phases involves three components:

1. A contaminant component consisting of the strength of binding between the contaminant and a surface site,

2. A solid phase component consisting of the number of adsorption sites,

3.   A solution component consisting of the concentration of cations competing for adsorption sites, anions that can form soluble aqueous complexes of the contaminant, pH, and oxidation-reduction (redox) potential.

Contaminant interaction with the geochemical environment can be modeled either very simply, or very complexly. Unfortunately, there is a fairly large gap between the two approaches, and not much I can come up with to bridge the gap. The simpler level is an isotherm approach. The more difficult approach is to use surface complexation theory in a geochemical reactive transport code.

The isotherm approach has been in use for many years at the INEEL and elsewhere, and is most commonly involves the use of a linear, reversible, equilibrium partition coefficient (Kd). A slightly more advanced isotherm approach is to relax the requirement that the adsorption isotherm be linear. Adsorption of uranium and neptunium is not linear, as shown by recent experiments conducted at Clemson University. A better, and slightly more complex, model of adsorption for uranium and neptunium would be a nonlinear, Freundlich isotherm. The isotherm approach (either linear or Freundlich) is already available in the TETRAD computer code. An isotherm approach generally lumps the three components governing adsorption (listed above) into one single number. Using the isotherm approach does not make factors 1 through 3 go away, it either ignores them, or assumes they are constant. Item two may be more explicitly evaluated, in some cases, if the isotherm is measured on a variety of materials, and the isotherm parameters assigned as a material property with possible spatial variability.

Surface complexation models apply the laws of chemical mass action to adsorption onto solids. Surface complexation models can be combined with geochemical computer models of solution chemistry to model adsorption and to account for system variables such as redox potential, pH, competing cations, and complexing ligands. This approach provides a much more robust ability to predict transport because more of the variables are explicitly accounted for. On the other hand, computational burden increases by many orders of magnitude because all the important geochemical factors in the system must be carried through the simulation, not just the contaminant. A geochemical reactive transport code is the only approach that would provide the ability to deal with strong geochemical gradients, such as for leachate released from pits and trenches.

Linear adsorption (Kd). At the simplest level, the distribution of a contaminant between aqueous and solid phases is quantified at thermodynamic equilibrium by the K_d, an empirically determined parameter. The K_d for a contaminant X is defined in Kipp, Stollenwerk, and Grove (1986) by:

$$K_d = \frac{[X]_s}{[X]_{eq}} \tag{1}$$

where

K_d =   distribution coefficient (ml/g)

$[X]_s$ =   contaminant sorbed per unit mass of material (mg/g or pCi/g)

$[X]_{eq}$ =   concentration of X in solution after equilibration with the solid material (mg/ml or pCi/ml).

A technique that has been somewhat more successful in accounting for spatial variability in adsorption uses a surface area based distribution parameter. Instead of a K_d in ml/g, an adsorption coefficient defined in terms of surface area can be defined as

$$K_A = \frac{K_d}{S_A}$$

(2)

where

K_A =   surface area distribution coefficient (ml/m^2)

S_A =   specific surface area (m^2/g).

Bertetti, Pabalan, and Almendarz (1998) found that when the K_d was normalized to a specific surface area for a range of materials, the surface area distribution coefficient showed much less variation than the mass based K_d. This partition coefficient is still based on linear, equilibrium, reversible adsorption.

Adsorption Isotherm. The linear K_d assumes that there is a linear relation between the concentration in solution and the adsorbed concentration. Not all adsorption sites have the same binding energy, and there are a finite number of adsorption sites available. Therefore, there is not always a linear relation between adsorbed and solution concentrations. A Freundlich isotherm (equation 3) can be used to model nonlinear adsorption behavior (Fetter 1993). A Freundlich isotherm is expressed by:

$$[X]_s = K_f [X]_{eq}^n$$

(3)

where

K_f =   Freundlich distribution coefficient

n =   constant.

As n approaches 1, sorption approaches linearity and K_f approaches the linear K_d.

Clemson University recently measured adsorption isotherms on fourteen sedimentary interbed samples collected inside and outside the SDA. For neptunium and uranium, isotherms showed distinct nonlinearity. A good fit to the actinides was obtained using a Freundlich isotherm. Figure 6 shows an example for neptunium adsorption on sample 7DS00501KD measured at Clemson University. The K values of the Freundlich isotherm showed a large amount of variation between different soil samples, but the exponents of the isotherms were very similar for all of the soil samples (see the Appendix to this memo for actual values). When plotted on a log-log graph, the Freundlich isotherm becomes linear. The Freundlich n is the slope of the curve. Parallel lines on the log-log plot indicate how similar the Freundlich n values are (Figure 7).
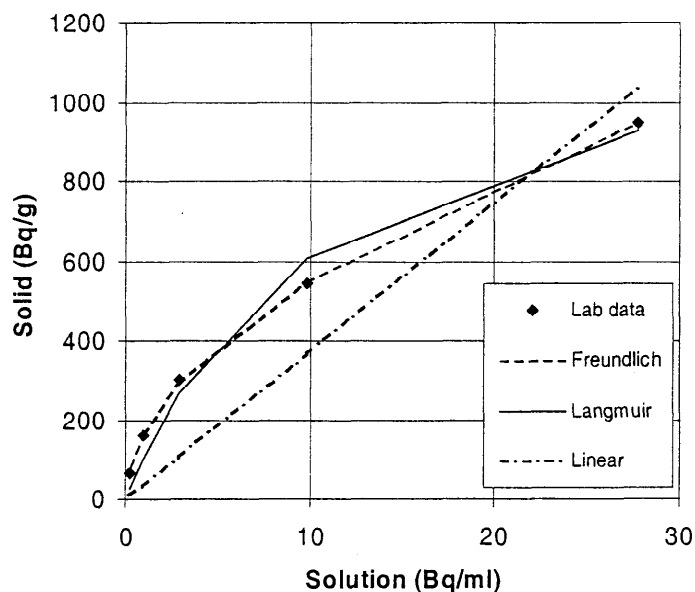
Figure 6. Graph of neptunium adsorption for sample 7DS00501KD comparing the fit of a Freundlich, Langmuir, and linear isotherms to the laboratory data.
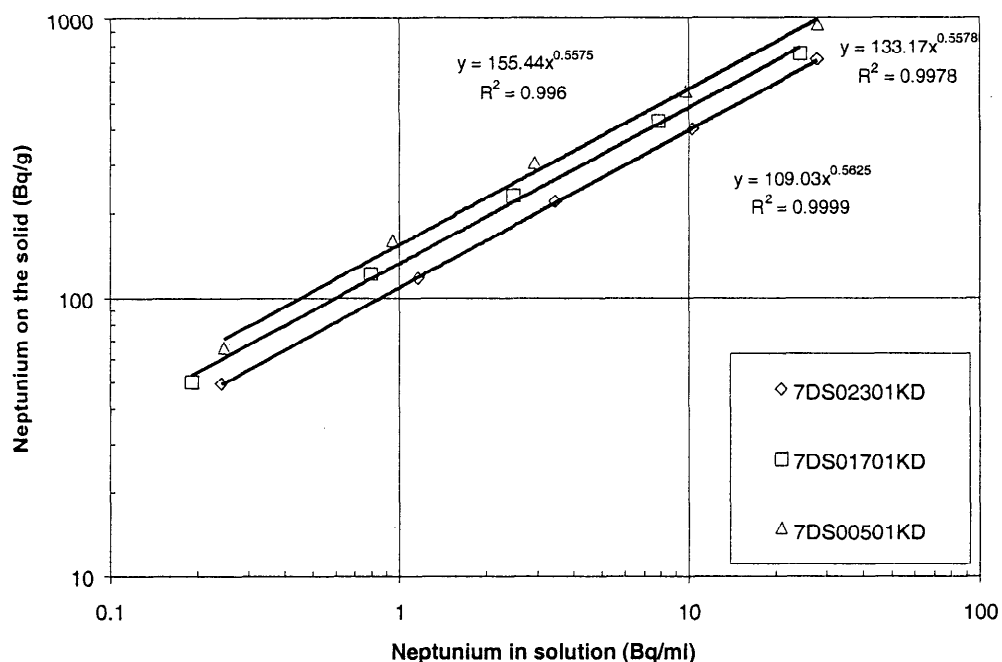

Figure 7. Graph of neptunium adsorption for three samples showing the similar slopes for the three soils when fit with a Freundlich isotherm.

Surface Complexation Models. More sophisticated approaches are needed that allow the assumptions of constant geochemical conditions to be relaxed. Surface complexation models are based on the assumption that the formation of complexes with functional binding sites on mineral surfaces is analogous to the formation of aqueous complexes in bulk solution. While there are several variations on surface complexation models, the diffuse layer model for adsorption is one of the simplest of the surface

complexation models that can still account qualitatively and quantitatively for the observed variation in experimental data (Dzombak and Morel 1990; Turner and Sassman 1996; Pabalan et al. 1998). The diffuse-layer model also is the model currently incorporated into the readily available geochemical computer simulation codes such as PHREEQC (Parkhurst and Appelo 1999) and Geochemist's Workbench (Bethke 1998).

Surface complexation is the formation of a chemical bond between an ion in solution (M^{+m}) and a reactive surface site on a mineral surface ($\equiv SOH^0$). Cations in solution form complexes with the surface site ($\equiv SOM^{+(m-1)}$) as described by a chemical mass-balance reaction:

$$\equiv SOH^0 + M^{+m} \leftrightarrow \equiv SOM^{+(m-1)} + H^+ \tag{4}$$

where the distribution of metal ion M^{+m} between the aqueous and solid phases at equilibrium is given by the equilibrium constant expression:

$$K_s = \frac{[\equiv SOM^{+(m-1)}][H^+]}{[\equiv SOH^0][M^{+m}]} \exp\left(\frac{-\Delta ZF\Psi}{RT}\right). \tag{5}$$

This reaction releases a hydrogen ion (H^+) into solution, and so the equilibrium between the free metal in solution and the adsorbed metal on the surface will depend on the pH. At low pH, the metal may not be able to replace a hydrogen ion on the surface, and adsorption will be decreased.

The number of adsorption sites will be given by the surface area of the material (S_A), times the number of adsorption sites per unit area (n), and is equal to the sum of the free and complexed surface sites.

$$nS_A = \equiv SOH^0 + \equiv SOM^{+(m-1)}. \tag{6}$$

The concentration of adsorbed metal [$\equiv SOM^{+(m-1)}$] is obtained by substituting Equation 6 into Equation 5 to replace $\equiv SOH^0$:

$$\equiv SOM^{+(m-1)} = \frac{K_s nS_A M^{+m}}{H + K_s M^{+m}}. \tag{7}$$

In addition to forming complexes with surface sites, the metal can form aqueous complexes with ligands (L^n) in solution. Formation of an aqueous complex also is a mass-balance reaction:

$$M^{+m} + L^{-n} \leftrightarrow ML^{+m-l} \tag{8}$$

with an equilibrium constant expression given by

$$K_l = \frac{[ML^{+m-l}]}{[M^{+m}][L^{-l}]}. \tag{9}$$

The total concentration of the metal M^{+m} in solution will be the sum of the free and complexed metal concentration

$$M_T = M^{+m} + ML^{+m-l}. \tag{10}$$

Solving Equation 9 for ML^{+m-l} and substituting into Equation 10 gives an expression relating the total metal concentration and the free metal concentration:

$$M_T = M^{+m} + M^{+m}K_l L^{-l} = M^{+m}(1 + K_l L^{-l}). \tag{11}$$

Combining equations for $\equiv SOM^{+(m-1)}$ and M_T in and simplifying gives an expression for adsorption that includes the effects of pH, surface area, and complexing ligands:

$$K_r = \frac{K_s n S_A}{[H + K_s M^{+m}][1 + K_l L^{-l}]}.$$ (12)

This mechanistic approach applies the concepts of chemical mass balance and mass conservation to adsorption. The approach can address pH effects, solution chemistry effects, and surface area effects on adsorption of metals or radionuclides onto minerals. This approach will permit addressing low or high pH values from waste solutions, complexing with organic chelating agents, and the formation of inorganic complexes with fluoride, phosphate, carbonate, or other ligands in solution. Figure 8 illustrates how the adsorption coefficient for a metal that forms an aqueous complex with a carbonate ion will vary as a function of pH and total dissolved carbonate concentration. The partition coefficient can vary over several orders of magnitude in the pH range of interest in the RWMC vadose zone (pH from 7.1 to 8.4). Figure 8 clearly illustrates the fallacy of using a single isotherm parameter for a system where the chemistry of the water is not constant.
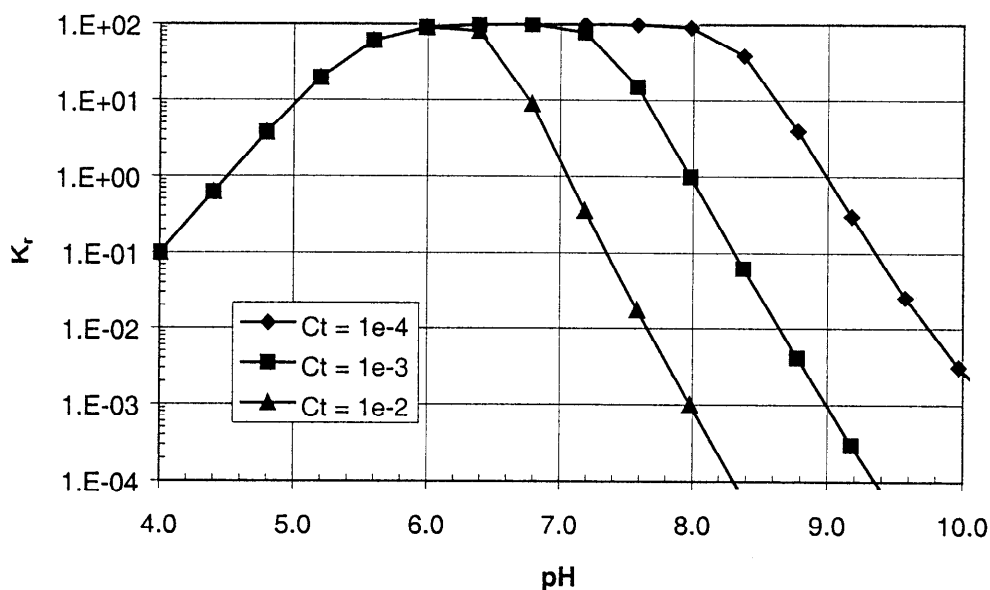

Figure 8 Graph of the partition coefficient (K_r) as a function of pH and total dissolved carbonate concentration (Ct) in moles/liter.

Geochemical codes deal with aqueous solutions and the interactions of the aqueous solutions with associated solid and gas phases. Such a code can be used to predict the fate actinides under the SDA including the effects of variable geochemical environments and steep geochemical gradients. A number of geochemical modeling codes have been developed over the past two decades to allow modeling of geochemical reactions in aqueous systems. Geochemical codes commonly in use by the geochemical community are PHREEQC, MINTEQA2, EQ3NR, and Geochemist's Workbench. Geochemist's Workbench is a commercially available geochemical reaction code. The code can calculate the equilibrium distribution of chemicals among aqueous species, minerals, gas phase, and adsorption sites on mineral surfaces. Geochemist's Workbench also has the ability to model kinetic reactions where equilibrium assumptions are not valid. With the inclusion of the flow model XT, Geochemist's Workbench can perform a limited simulate advection of contaminants. Geochemical computer codes solve a system of equations representing geochemical reactions. All codes require a set of input data

consisting of a suite of geochemical mass action equations and the equilibrium constants that describe those reactions. The results of the geochemical modeling can be no better than the quality of the input thermodynamic data.

Incorporation of Geochemistry Into Transport. A linear adsorption coefficient is very simple to incorporate into a transport model. The linear isotherm results in a simple, linear retardation of a contaminant relative to the movement of water. Transport can be calculated from the water movement simply by multiplying by a scaling factor. A nonlinear isotherm is a little more involved, but is still fairly simple to implement. The nonlinear isotherm requires iteration to a solution for each node and time step. To account for spatial variability, the adsorption parameters can be assigned as material properties rather than as contaminant properties. The material property is then distributed through the model as any other material property would be distributed.

Including geochemical reactions permits addressing spatial variation in geochemical environments, but carries a very much higher computational burden. To account for the chemistry of the solution, all of the important solutes need to be simulated, not just the contaminant. Reactions with solid phases must be explicitly included. Computation of complicated geochemical models is generally limited to small systems or to one dimension. It would be possible to use a flow model to define flow lines from waste to the aquifer. A reactive transport model could then be used in one-dimension along this flow line to include the full suite of geochemical reactions anticipated from the waste to the aquifer.

The Need for Site Specific Data

Site-specific actinide-migration parameters are needed for the RWMC risk assessment. Motivation for this statement comes from EPA national policy and external technical review of the interim risk assessment for OU 7-13/14. Site specific partition coefficients are specified for risk assessment in written EPA policy "...partition coefficient values measured at site-specific conditions are absolutely essential." (EPA 1999). The USGS review of the interim OU 7-13/14 risk assessment concluded that partition coefficients that were not measured under site-specific conditions could not be shown to be representative or conservative (USGS 2000).

Recommended Course of Action

For the OU 7-13/14 risk assessment and record of decision, a simple approach using an adsorption isotherm is recommended. However, the parameter used for the isotherm must be defensible as representative and also should probably be conservative. This can be done by measuring site specific adsorption coefficients (linear Kd or nonlinear Freundlich) on a range of interbed sediment materials collected at the SDA in water that is similar to water in the vadose zone under the SDA. Using water representative of the vadose zone, factors such as pH, competing cations, and complexing anions can be empirically included in the measured parameter. By using a range of samples, a range of adsorption parameters can be determined. The distribution will show how much variation there is. A number can be selected from near the bottom of the range. This number will be representative (since it is from the observed range) and conservative (since it is from near the bottom of the range).

For uranium and neptunium, a nonlinear isotherm is the recommended approach. However, this will cost twice as much as measuring a linear partition coefficient (it takes five points to define the isotherm as opposed to three replicates at one point for the linear partition coefficient). This will not appreciably affect the computational burden, and TETRAD includes the capability of nonlinear adsorption. If isotherms were measured for uranium and neptunium on the 24 SDA interbed samples currently awaiting analysis at INTEC, in the two representative waters, we would have three data sets on adsorption isotherms measured in three different solutions. This would provide a sound basis for determining representative and conservative.

Americium does not break through in column experiments, but does seem to have a small highly mobile fraction. Valence is not an issue with americium. The recommendation is to measure linear Kd partition coefficients for americium in the two representative vadose zone waters on the 24 interbed samples. This will provide a set of representative Kd values for americium. The facilitated transport issue seems more significant for americium than whether the isotherm is linear or not.

Plutonium has both facilitated transport issues and may have valence state issues. It seems reasonable to assume that plutonium will be reduced to plutonium (IV) in the vadose zone under the SDA (if not in the waste itself). However, since plutonium (VI) has a much higher mobility (lower Kd value), the regulators may have difficulty accepting a Kd of 5100 ml/g (which is based on plutonium (V) being reduced to plutonium (IV) during adsorption and column experiments). Kd values as low as 110 ml/g have been measured for plutonium (VI). My first recommendation is to hire or subcontract your own expert to support the position that plutonium (IV) is going to be present in the vadose zone to include in the risk assessment report. The second recommendation is to measure linear Kd partition coefficients for plutonium (IV) in the two representative vadose zone waters on the 24 interbed samples. This will provide a set of representative Kd values for plutonium. The facilitated transport issue seems more significant for plutonium than whether the isotherm is linear or not.

For facilitated transport, several studies have determined a small, highly mobile fraction of americium and plutonium in column studies. This will need to be incorporated into the risk assessment. However, as we currently have data from 6 inch columns, there is a certain amount of trepidation in extrapolating the results directly to 500 feet. I do not believe an empirical factor developed at 6 inches could stand scrutiny for extrapolation to 500 ft. To make this approach credible, I believe that an analysis of facilitated / colloidal transport mechanisms needs to be performed. A mechanism that would provide the observed column results needs to be identified. This mechanism could then be extrapolated to the field scale problem. I recommend that an expert on colloidal transport of radionuclides be hired or subcontracted to develop a mechanism, and then develop the parameters for the model based on the column data and the mechanism.

To develop a defensible simulation model incorporating spatial variability in geochemical material properties cannot be done with the available data or data that is planned to be gathered in the next few months. Swen Magnuson has been evaluating the spatial distribution of hydrologic material properties to incorporate into the baseline risk assessment. He has found that it takes something on the order of 80 observations of a property before there is sufficient data to estimate spatial distribution. The current plan calls for only 22 locations to be characterized for transport properties. This will not be enough to to any spatial distribution analysis. I recommend for the time available between now and September 2001 that you stick with average properties for geochemistry.

This recommended approach for the near-term risk assessment to reach the record of decision (ROD) still contains appreciable uncertainty. The biggest assumption in this approach is that there are no significant changes in the subsurface geochemistry either spatially or temporally. A more sophisticated analysis conducted in parallel to the monitoring after the ROD would further refine the geochemical evaluation. Characterization data and monitoring data will allow actual geochemical environment parameters to be incorporated into the model. The more advanced geochemical modeling would be used to interpret the monitoring data and to allow assessment of the monitoring data in terms of compliance with the conditions of the ROD. If a one- or two-dimensional reactive transport model was used for a very limited area, it could provide significant support for interpretation of future 5 year reviews.

Table 6. Recommended course of action to incorporate geochemistry into risk assessment models.

Assume now through September 2001	Tasks to validate short-term assumptions up to draft Record of Decision	Long term approach and tasks to validate position for 5 year review of ROD
Redox		
Based on 1988 dissolved oxygen measurements, assume the vadose zone is oxidized. Assume U is U(VI), Np is Np(V), Pu is Pu(IV), and Am is Am(III)	Measure O_2 and CO_2 in the vadose zone gas phase using VVE observation ports. Measure DO and dissolved organic carbon in perched zone and lysimeter water samples Literature review of actinide valence states, particularly in contact with sediments. Limited thermodynamic calculations. Hire an expert (like Greg Choppin, Florida State Univ.) to evaluate this position and prepare something for the BRA report.	Periodic resampling to evaluate possible trends in redox conditions, particularly if leachate from pits and trenches is appearing in lysimeters and perched water. Sample water from lysimeters installed in waste. Selective extraction of radionuclides for determination of valence state. Explicitly include measured redox conditions and changes in redox conditions between waste and the underlying vadose zone in a reactive transport simulation.
Organic complexing		
In the absence of data, assume no organic complexes are present in the vadose zone.	Measure citrate, oxalate, and EDTA in perched water and lysimeter samples under the SDA. Literature review to evaluate the persistence of these organic chemicals in the environment.	Measure citrate, oxalate, and EDTA in lysimeter samples collected from inside pits and trenches. Literature search to find formation constants for chelating agents with actinides. Explicitly include formation of organic complexes (if measurements show they are present) in a reactive transport simulation.
Inorganic complexing		
Assume current data base of site specific partition coefficient values have been measured in synthetic water that adequately incorporates the effect of anion complexing.	Perform geochemical computer modeling of speciation of actinides in various water chemistries. Simulate formation of surface complexes in various waters to quantitatively evaluate the effect of water chemistry on adsorption. Use geochemical models to test the hypothesis that the available data are	Perform adsorption studies as a function of water chemistry. Develop parameters for geochemical surface complexation models and ion exchange models from laboratory data. Simulate the effect of chemistry on adsorption.

Assume now through September 2001	Tasks to validate short-term assumptions up to draft Record of Decision	Long term approach and tasks to validate position for 5 year review of ROD
	conservative. Perform batch adsorption measurements in representative SDA water chemistry with high TDS and low TDS as measured in suction lysimeters.	
Competing Cations		
Assume current data base of site specific partition coefficient values have been measured in synthetic water that adequately incorporates the effect of competing cations.	Perform geochemical computer modeling of speciation of actinides in various water chemistries. Simulate formation of surface complexes in various waters to quantitatively evaluate the effect of water chemistry on adsorption. Use geochemical models to test the hypothesis that the available data are conservative. Perform batch adsorption measurements in representative SDA water chemistry with high TDS and low TDS as measured in suction lysimeters.	Perform adsorption studies as a function of water chemistry. Develop parameters for geochemical surface complexation models from laboratory data. Simulate the effect of chemistry on adsorption.
Uniform properties versus spatial distribution		
Divide the domain into basalt and sediment layers. Assume uniform material adsorption properties throughout each material type in the model domain.	Assume uniform material properties throughout the model domain. Compile existing data on partition coefficients and study frequency distributions. Select partition coefficients from distributions that are representative but conservative.	Measure distributed material properties on samples from existing wells and new wells. Using spatial analysis techniques such as kriging to estimate the spatial distribution of retardation properties of sediments.
Isotherm versus Kd		
Some adsorption isotherms have been measured for uranium and neptunium. The isotherms are very nonlinear. With this data, there is evidence that the adsorption is nonlinear. There are 14 adsorption isotherms measured on samples from inside and outside the SDA. Use this database to establish a single	Use geochemical modeling and the water chemistry used to measure the adsorption isotherms to verify that the results will be reasonably conservative with respect to water chemistry.	Measure parameters for a surface complexation and ion exchange model of reactive transport. Use mechanistic model to calculate adsorption coefficients. Perform additional laboratory experiments to develop adsorption parameters for mechanistic models.

Assume now through September 2001	Tasks to validate short-term assumptions up to draft Record of Decision	Long term approach and tasks to validate position for 5 year review of ROD
representative, yet conservative isotherm for uranium and neptunium.		

Colloids or facilitated transport

Assume now through September 2001	Tasks to validate short-term assumptions up to draft Record of Decision	Long term approach and tasks to validate position for 5 year review of ROD
Using results of experiments at Clemson, develop an empirical release fraction or release rate of a highly mobile fraction of plutonium and americium. Set up TETRAD to transform some small fraction of normal Pu and Am to a highly mobile fraction with a small retardation factor. Using results of experiments at Clemson, develop retardation factors for highly mobile fraction of americium and plutonium.	Acquire through hiring action or subcontract an expert in colloidal transport (such as Markus Fleury of Washington State Univ). Develop a mechanistic model of colloidal transport. Use the Clemson column results to verify the mechanistic model. Use this mechanistic hypothesis in the baseline risk assessment as the justification for the approach taken to plutonium and americium transport.	Develop and perform a series of experiments to test the hypothesis developed for the baseline risk assessment. Use the experimental results and mechanistic model to improve the algorithms used to model colloidal transport and to improve the parameters used in models.

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